Predicting and Mapping Herbicide-Soil Partition Coefficients for EPTC, Metribuzin, and Metolachlor on Three Colorado Fields

Dale L. Shaner, Hamid J. Farahani, and Gerald W. Buchleiter*

Understanding the spatial variability of herbicide sorption to soil is important in determining the bioavailability as well as leaching potential of the chemical across a field. Multiple methods have been used to estimate herbicide sorption variability at the macroscale, but it has been difficult to measure soil heterogeneity or herbicide sorption at the individual field level. One method to determine soil heterogeneity is to create zones within a field based on maps of the apparent bulk soil electrical conductivity (ECa). These zones can be used to direct soil sampling to determine the fraction of organic carbon (f_{oc}) of each zone. The f_{oc} , in turn, can be used to predict the variability of herbicide binding among zones. Surface (0 to 30 cm) bulk-soil electrical conductivity (EC_s) maps were made for three sandy fields in eastern Colorado, and soil samples were taken from the EC_s zones within each field. The f_{oc} and the soil–water partition coefficient (K_d) for EPTC, metribuzin, and metolachlor were determined for each sample. There were significant correlations between EC_s and f_{oc} (R) = 0.75) and between f_{oc} and K_d for EPTC, metribuzin, and metolachlor (R = 0.66, 0.61, and 0.71, respectively) across all three fields. Additional soil samples taken from the ECs zones located in previously unsampled areas of the three fields showed that one could reasonably predict $K_{
m d}$ values for metribuzin, metolachlor, and possibly, EPTC based on the $f_{
m oc}$ zones derived from EC_s maps.

Nomenclature: EPTC; metolachlor; metribuzin.

Key words: Precision agriculture, electrical conductivity, herbicide-soil partition coefficient, soil.

Herbicides are the major pesticide input in agriculture in terms of volume and market share. Soil-applied herbicides continue to be widely used in many crops. Atrazine and an acetanilide were applied to 66 and 57%, respectively, of the total corn (Zea mays L.) area in the United States in 2005 (NASS, 2006). Approximately 20% of the soybean [Glycine max (L.) Merr.] area and more than 80% of the cotton (Gossypium hirsutum L.) and potato (Solanum tuberosum L.) areas received a soil-applied herbicide in 2005 (NASS, 2006).

The activity and fate of soil-applied herbicides are affected by multiple factors, including soil organic matter (SOM), pH, cation-exchange capacity (CEC), and texture (Blackshaw et al. 1994; Cheng, 1990), which affect the adsorption of the herbicide to the soil. The adsorption of herbicides to the soil determines the bioavailability of the chemical to both weeds and soil microbes. As SOM increases, additional atrazine is needed to maintain weed control (Blumhorst et al. 1990), and the efficacy and mineralization of atrazine and alachlor can vary across a field depending on soil properties (Liu et al. 2002).

The variability of herbicide adsorption and bioavailability at the regional and field level has been studied with the goal of identifying soils that are more vulnerable to herbicide leaching. Novak et al. (1995) and Wood et al. (1987) found that the sorption of atrazine and metolachlor was spatially variable and that the sorption of both herbicides was related to SOM, pH, and clay content. Williams et al. (2002) reported that the bioavailability of isoxaflutole varied across a field and was related to clay and SOM variability.

The most sensitive input parameter in many herbicide fate and transport models is the soil water-herbicide partitioning coefficient (K_d). Attempts to model the variability of herbicide K_d have relied on either intensive sampling or soil and topographical maps. Macur et al. (2000) used either detailed rates of isoxaflutole within a county, the resolution was too coarse to be applied at the field level. Novak et al. (1997) found that field scale maps based on landscape position was more effective than soil series maps for predicting atrazine sorption. Farenhorst et al. (2003) reported that a combination of topography and soil property data were appropriate for predicting the spatial distribution of 2,4-D adsorption. Two of the obstacles faced in all of these approaches are either that they do not work well at the individual field level or that the level of sampling is cost prohibitive. Multiple methods have been used to measure the variability of soil across a field (Goodwin and Miller 2003). Apparent bulk-soil electrical conductivity (EC_a) has become one of the most frequently used methods to measure soil variability within a field because of its ease of use and reliability (Corwin and Lesch 2003). Soil ECa has been shown to be an indicator

soil profile characterization or the 1:24,000 scale, U.S.

Department of Agriculture-National Resource Conservation

Service (USDA-NRCS) Soil Survey database coupled with

parameter estimations to predict solute transport using two

different transport models. They found that the detailed soil

profile characterization gave a better estimate of solute

transport compared with the soil survey database. Williams

et al. (2002) attempted to estimate the efficacy of isoxaflutole

by using NRCS soil maps. Although they could draw large-

scale maps that indicated the potential for using differential

Soil EC_a maps are increasingly being used to direct soil sampling (Bronson et al. 2006; Doerge et al. 2006.) The assumptions in using zone sampling, particularly that based on soil EC_a maps, are that the soil contained within an EC_a zone is similar, and that one can extrapolate from a relatively small number of samples taken within a zone to other areas within that zone.

of multiple soil properties, including soil moisture, clay, salinity, pH, CEC, and SOM (Rhoades, 1993; Sudduth et al.

1995, Corwin and Lesch 2005).

Soil EC_a maps have successfully mapped soil types within a field. Anderson-Cook et al. (2002) found that EC_a correctly classified soils into two broad categories with greater than

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^{*}U.S. Department of Agriculture-Agricultural Research Service, (USDA-ARS), Water Management Research Unit, 2150 Centre Ave, Building D, Suite 320, Fort Collins, CO 80526; Corresponding author's E-mail: dale.shaner@ars.usda.gov

85% accuracy. Several researchers have related soil EC_a to variation in crop production caused by soil differences (Jaynes et al. 1995a; Kitchen et al. 2003; Zhang and Taylor 2001).

Jaynes et al. (1995b) determined the relationship among EC_a and the fraction of organic carbon (f_{oc}) and the K_d for atrazine. The correlation coefficient between K_d and EC_a was 0.575 and between f_{oc} and EC_a was 0.686. All of these properties were spatially variable within the field. They concluded that EC_a maps could be used to estimate the variability of f_{oc} in a field, and the f_{oc} , in turn, could be used to estimate the differences in leaching potential of atrazine across a field. Although this method sounds promising, there are few, if any, published studies that have used soil EC_a maps to estimate herbicide K_d variability of multiple herbicides across a number of fields.

Three soil-applied herbicides that are widely used in Colorado and throughout the United States are EPTC, metribuzin, and metolachlor. Approximately 74 and 24% of the potato area in the United States was treated with metribuzin and EPTC, respectively, in 2005 (NASS, 2006). Metolachlor was applied to 23% of the corn area in the United States in 2005 (NASS, 2006). These three herbicides bind differently to the soil. The average organic carbon partition coefficient (K_{oc}) are 200, 60, and 200 for EPTC, metribuzin, and metolachlor, respectively (Weber et al. 2000).

The objectives of this research were (1) to determine the relationship between mapped surface (0 to 0.3m) bulk-soil electrical conductivity (EC_s) zones within a field and the f_{oc} and the $K_{\rm d}$ of EPTC, metribuzin, and metolachlor to soil from three different fields in Colorado; and (2) to examine whether the relationship between mapped EC_s zones and f_{oc} could be used to predict the $K_{\rm d}$ of these three herbicides in other parts of the EC_s zones within a field that had not been previously sampled.

Materials and Methods

Sample Sites. This study was conducted as part of a multidisciplinary precision-farming research project (Heermann et al. 2002). Three fields irrigated by center pivots under conventional tillage were used in this project. Two were located near Wiggins, CO (designated as Wiggins1 and Wiggins2), and one near Yuma, CO (designated as Yuma). Wiggins1 and Wiggins2 are 71 and 52 ha, respectively, and are located a few kilometers apart. The soils in these two fields include a Bijou loamy sand (coarse loamy, mixed, superactive, mesic Ustic Haplargids), Valentine sand (sandy, mixed, nonacid, mesic Typic Ustipsamments), and Truckton loamy sand (coarse loamy, mixed, superactive, mesic Aridic Argiustolls). Yuma is 57 ha and includes Haxtun loamy sand (fine-loamy, mixed, superactive, mesic Pachic Argiustolls), Albinas loam (fine-loamy, mixed, superactive, mesic Pachic Argiustolls), and Ascalon fine sandy loam (fine-loamy, mixed, superactive, mesic Aridic Argiustolls).

EC_a Measurements. Measurements of EC_a were taken in 1999 in Wiggins1 and Wiggins2, and in 2000, in Yuma using the Veris 3100 Soil EC Mapping System. The Veris unit has six coulter electrodes mounted on an implement that can be pulled by a pickup truck. It uses a modified Wenner configuration to measure EC_a by inducing a current in the soil through two coulter electrodes and measuring the voltage

drop across the two pairs of coulters that are spaced to measure EC_a (Lund et al. 2000). During field measurements, the coulters penetrate the soil 20 to 50 mm. The Veris system interfaces with a differential geographical positioning system (GPS) and provides simultaneous and georeference readings of EC_a for both surface (0 to 0.3 m; EC_s) and deep (0 to 0.9 m; EC_d) depths. Measurements were taken in the spring before tillage and planting. Travel speeds through the field ranged between 7 and 16 km h⁻¹ with measurements taken every second, corresponding to 2 to 4 m spacing between measurements in the direction of travel, respectively. A parallel swather, mounted inside the truck, guided parallel passes through the field at 12 to 18 m swath widths with a GPS unit with submeter accuracy providing spatial coordinates for each EC_a measurement.

Construction of Soil Zone Maps. Although this research was focused on the 0- to 0.3-m soil depths, different soil environments within a field may have similar surface-soil attributes. Therefore, we used whole-profile ECa attribute patterns to identify different soil environments. For locating all sample sites, we considered ECa zones based on ECs and EC_d patterns identified through cluster analysis and the ESAP-95 software (see following section). Preliminary analysis of the resulting data indicated that in these fields f_{oc} and soil texture attributes of the surface were most strongly related to EC_s. EC_d patterns either followed the EC_s patterns or did not modify or add additional information in the relationship of the surface soil attributes to EC_s. So for the exploration of the K_d , f_{oc} , and EC_s relationships, EC_s zones based on patterns were identified in cluster analysis of EC_s data only. Each sample site was then assigned to a ECs zone.

The SAS Ward's clustering algorithm (SAS 2001) was used on EC_s for the EC_s zones, whereas normalized (to a mean of 0 and standard deviation of 1) soil EC_s and EC_d data were used for the EC_a zones. This algorithm forms clusters by successively joining sites or clusters at each iteration of the algorithm so that the newly formed cluster minimizes the within-cluster variance and maximizes the between-cluster variance. The choice of the number of soil EC_s zones was based on cluster statistics generated by the clustering algorithm and subsequent exploration of EC_s and EC_d data distributions over the clusters and the spatial aggregation and location of clusters in the field.

Zone maps were developed from the cluster membership of the EC_s sites. The soil EC_s data were spatially dense, so a raster-cell map was created by the proximity function in ArcView software.⁵ The proximity function in ArcView identifies the area represented by each sample point relative to its neighboring sample points and assigns a class membership to that area. The noisiness of this map is reduced by a moving-window neighborhood analysis, which assigns the majority class of a 5 by 5 cell block to the center cell of that block. Final zone delineations were based on spatially aggregated cells of the same cluster membership. Small area delineations that would not be included in a management zone map were maintained in the maps used for locating sample sites.

Soil Sample Site Location. Sample site locations were based on EC_s and EC_d patterns within each field. The ESAP-95 computer program (Lesch et al. 2000) was used to identify 23

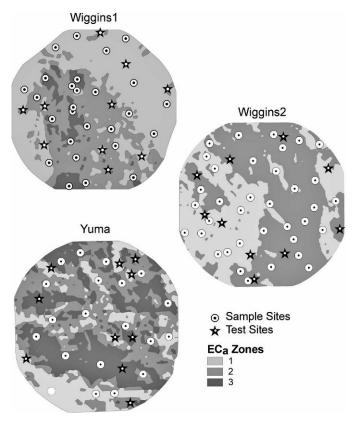


Figure 1. Maps of shallow (0-30 cm) soil bulk-soil electrical conductivity (ECs) zones of Wiggins1, Wiggins2, and Yuma, CO. Light to dark grey indicate increasing ECs values for the zones. O, sites of original samples A, sites of test samples.

and 24 soil-sampling locations across the measured soil ECs and EC_d maps for Wiggins1 and Wiggins2, respectively. This software is designed to locate sample sites over the spatially distributed range of predictor values in such a way as to eliminate spatial autocorrelation in the residuals of a regression analysis. In the Wiggins fields, the sites tended to be located at the field edges, at the edge of the soil ECa zones, or certain areas of the field had no sample sites located. In the interest of characterizing zones, we located an additional 4 and 14 soilsample locations in Wiggins1 and Wiggins2 study sites, respectively. The additional soil-sampling sites were identified by inspection of soil EC_a zone maps (see next paragraph), thereby generating a total of 27 and 38 soil sample locations at Wiggins 1 and Wiggins 2, respectively (Figure 1). Soil samples were taken in March 2000.

At Yuma, a total of 20 sample locations where identified using the EC_a data with location selection based on inspection of EC_a cluster-based zone maps. The location of these 20 sample sites, the additional Wiggins sample sites, and the follow-up samples in all fields were based on ECa zone maps using the following process and criteria: (1) A major objective in locating sample sites in each EC_a class was to place the sites in different delineations of the ECa class, which were dispersed over the field and covered the range of delineation contexts (such as delineation size, shape, and class membership of adjacent delineations); (2) Some large delineations purposely had more than one sample located in it, and in these delineations, an attempt was made to separate sites by distance and intervening areas of greater class membership variation, and in some cases, to place them in areas of different subclasses of the delineation; and (3) In addition to the zone delineation map, the point data of site-class membership was used to place the sample site in localities with relatively homogenous classification. The third criteria meant that sample sites were located away from delineation boundaries, although how close the site was to a boundary depended on the size or shape of a delineation. Soil samples were taken in March 2001.

After the initial analysis of the soil and binding of herbicides to the original samples from each field, 10 additional sites were chosen in 2003 from each field as sample areas that had not previously been examined but were in distinct EC_a zones (Figure 1). An attempt was made to sample EC_s zone sites that were isolated from the original sample sites but were classified within the same zone.

Soil Sampling and Analysis. The EC_a values for each of the soil samples were determined by averaging the ECa values taken within an 8-m radius of each sample site with a minimum of three ECa values for each sample site. The numbers of samples taken were 28, 38, and 20 from Wiggins1, Wiggins2, and Yuma, respectively. Sites were located with a GPS unit with submeter accuracy. Two soil cores (0.05 m diameter by 1 m) were taken from each sampling location and were composited by soil horizon. Lab analyses were done by horizon, and the results were then depth-weighted to put the soil attribute data on a 0.3-m depth basis. Only the 0- to 0.3-m attributes are used in this study. Samples were air-dried, ground, and sieved through a 2-mm mesh. Total soil carbon was determined on a combustion furnace analyzer (Nelson and Sommers, 1982). Inorganic C was measured using a modified pressure-calcimeter method (Sherrod et al. 2002). Soil organic C was calculated as total C from dry combustion minus inorganic C. (Nelson and Somers 1982; Sherrod et al. 2002).

Herbicide-Binding Measurement. The binding of analytical grade EPTC, metribuzin, and metolachlor to soil was determined for each sample. Ten g of air-dried soil was placed in a 50 ml centrifuge tube with a Teflon-lined cap.8 Ten milliliters of a 0.02 M CaCl₂ solution containing a herbicide at a concentration of 1 µg ml⁻¹ was added to each tube and the tube was shaken for 24 h. Preliminary studies showed that equilibrium had been reached after that time period. The samples were removed from the shaker and centrifuged for 20 min at 2,000 \times g. Three milliliters of the equilibrium solution supernatant was transferred to a 10-ml test tube, which had a Teflon-lined cap, and 3 ml of watersaturated toluene was added. The tube was shaken for 1 h and then centrifuged for 5 min at 1,000 \times g to separate the layers. The toluene phase was transferred to a 2-ml volumetric flask to which 10 µl of a 0.1 mg ml⁻¹ butylate internal standard solution was added.

The herbicide concentrations in the toluene phase were analyzed using a gas chromatograph equipped with a mass and monitoring masses for butylate spectrometer⁹ (mass: charge ratio [m/z] 146), EPTC (m/z 128), metribuzin (m/z 198, 199, 214), and metolachlor (m/z 162, 238). An HP 5 MS 30 mm by 0.25 mm column was used at a flow of ultrapure helium at 1.5 ml min⁻¹. The injection temperature was 250 C, and the detector temperature was 280 C. The program for separating the herbicides was to start the oven temperature at 80 C and hold for 1 min, then ramp at 20 C

Table 1. Descriptive statistics for 86 measurements of apparent soil electrical conductivity (EC_a), mass fraction organic carbon (f_{oc}), and herbicide-partition coefficient (K_d) for EPTC, metribuzin, and metolachlor.

						Correlation ^a				
			Ran	nge			$K_{\rm d}$			
Property	Mean	SE	Maximum	Minimum	f_{oc}	EPTC	Metribuzin	Metolachlor		
$EC_a (mS m^{-1})$	19.3	1.1	42.0	5.2	0.75	0.58	0.54	0.63		
$EC_a (mS m^{-1})$ $f_{oc} (g C 100 g soil^{-1})$ $K_d (L kg^{-1})$	0.59	0.23	1.27	0.27		0.66	0.64	0.71		
EPTC	0.88	0.04	1.81	0.25						
Metribuzin	0.26	0.02	0.80	0.00						
Metolachlor	1.20	0.06	2.73	0.33						

^a Correlations are significant at $P \le 0.05$.

min $^{-1}$ to 230 C and hold for 2.5 min with a run time of 11 min. Under these conditions, the retention times of butylate, EPTC, metribuzin, and metolachlor were 5.44, 5.95, 8.78, and 9.45 min, respectively. The detection limit was 0.01 μg ml $^{-1}$ for each herbicide. Quality control samples, included in every run, showed greater than 95% recovery of EPTC, metribuzin, and metolachlor by toluene from water.

The amount of herbicide sorbed by the soil was determined by the difference between the initial concentration of herbicide in the soil solution and the final concentration after equilibrating with the soil. The $K_{\rm d}$ was calculated as

$$K_d = [herbicide \ sorbed \ to \ soil(\mu g \ g^{-1})]/$$

$$[herbicide \ in \ solution(\mu g \ ml^{-1})]$$
[1]

 K_{oc} for each herbicide was calculated as

$$K_{oc} = K_{\rm d}/f_{oc} \times 100$$
 [2]

 f_{oc} is the soil organic C mass-fraction 100 g soil⁻¹ that was measured for each soil sample.

The range of K_d values in each EC_s zone was calculated as

$$K_{\rm d} = (K_{oc} \times f_{oc})/100$$
 [3]

The K_{oc} values used were the average values published in the literature (Weber et al. 2000), which were 200, 60, and 200 for EPTC, metribuzin, and metolachlor, respectively.

Statistical Analysis. ANOVA, t test comparisons, and Pearson correlation coefficients among K_d , EC_s, and various soil properties were calculated using SigmaStat ver. 3.5.¹¹

Results and Discussion

Correlation between EC_a, f_{oc} , and K_d for EPTC, Metribuzin, and Metolachlor. The EC_s values ranged between 5.2 and 42.0 mS m⁻¹ (Table 1) across all three fields. These values are only relative, however, and are not direct measures of the true soil electrical conductivity (Lesch et al. 1992). The f_{oc} ranged between 0.27 and 1.27 g C 100 g soil⁻¹ (Table 1). The correlation across all soil samples between EC_s and f_{oc} was 0.75 (Table 1), which is similar to that reported by other researchers (Corwin and Lesch 2005; Domsch and Giebel 2004; Jaynes et al. 1995b; Sudduth et al. 1995).

The $K_{\rm d}$ for EPTC, metribuzin, and metolachlor across all soil samples ranged between 0.25 and 1.81, 0.0 and 0.8, and 0.33 and 2.73 kg L⁻¹, respectively (Table 1). The correlation between $K_{\rm d}$ for EPTC, metribuzin, and metolachlor, and f_{oc} was 0.66, 0.64, and 0.71, respectively (Table 1). The average

 K_{oc} for EPTC, metribuzin, and metolachlor across all samples was 147 ± 43 , 37 ± 27 , and 192 ± 58 , respectively, which agree with the range of published values (Weber et al. 2000).

These results are consistent with other studies that have measured similar values for K_d for these three herbicides and have shown that one of the primary soil attributes that determine the binding of EPTC, metribuzin, and metolachlor is SOM (Daniel et al. 2002; Liu et al. 2000; Patakioutas and Albanis 2002; Singh 2006; Weber et al. 2000).

Relationship between EC_s Zones, f_{oc}, and Herbicide Binding. Cluster analysis resulted in three EC_s zones in Wiggins1 and Yuma and two zones in Wiggins2 (Figure 1). Farahani and Buchleiter (2004) found that the EC_a zones in these fields are very stable over time, although the actual EC_a values between measurements were different depending on the moisture content of the soil at the time of sampling.

One of the hypotheses in this study was that different EC_s zones within a field represent difference in soil characteristics, which, in turn, will bind herbicides differently. To characterize the soil within each zone, multiple samples were taken from each zone based on sampling sites that were dispersed over the field and covered a range of delineation contexts. The underlying assumption in using zone soil sampling is that soils contained within a zone are similar and that one can extrapolate from a relatively small number of samples taken within a zone to other areas within that zone.

In Wiggins1, there was a significant difference in the original samples in f_{oc} and the $K_{\rm d}$ for EPTC and for metolachlor among the three EC_s zones (Table 2). However, the $K_{\rm d}$ of metribuzin was not different between the EC_s zone 1 and 2, but there was a difference between zones 1 and 2 vs. zone 3 (Table 2). In Wiggins2, there were significant differences in the original samples in f_{oc} and the $K_{\rm d}$ for EPTC and metolachlor between the two zones but not for metribuzin $K_{\rm d}$ (Table 2). In Yuma, there was a significant difference in f_{oc} and the $K_{\rm d}$ for EPTC and metolachlor between zones 1 and 3, whereas zone 2 was intermediate between zones 1 and 3 (Table 2). Metribuzin $K_{\rm d}$ was significantly different between EC_s zone 1, and zones 2 and 3, but there was no significant difference in the $K_{\rm d}$ for metribuzin between zones 2 and 3 (Table 2).

EC_s was highly correlated with f_{oc} in all three fields, and the $K_{\rm d}$ for EPTC and metolachlor were correlated with f_{oc} in each of the fields (Table 3–5). The $K_{\rm d}$ for metribuzin, on the other hand, was not correlated with f_{oc} in Wiggins2 or Yuma (Tables 3–5). Metribuzin binds very weakly to soil (Daniel et al. 2002; Locke et al. 1994), and these data show that there was little difference in the binding of metribuzin across the

Table 2. Values of soil apparent electrical conductivity (EC_a), soil organic matter (f_{oc}), and herbicide-partition coefficient (K_d) values for EPTC, metribuzin, and metolachlor in different EC zones in Wiggins1, Wiggins2, and Yuma, CO. a,b,c

Field		EC zone	n	EC_a	f_{oc}	$K_{ m d}$			
	Sample type					EPTC	Metribuzin	Metolachlor	
				$mS m^{-1}$	g C 100 g soil ⁻¹		L kg ⁻¹		
Wiggins1	Original sample	1	11	9.1	0.41 c (0.35–0.46)	0.63 c (0.53–0.74)	0.07 b (-0.02-0.16)	0.74c (0.56–0.93)	
		2	11	16.2	0.58 b (0.52–0.64)	0.95 b (0.85–1.05)	0.20 b (0.11–0.29)	1.19 b (1.01–1.37)	
		3	5	25.0	0.81 a (0.76–0.87)	1.50 a (1.35–1.66)	0.49 a (0.36–0.62)	2.00 a (1.74–2.28)	
	Test sample	1	5	10.0	0.35*	0.56*	0.19	0.93*	
		2	5	17.8	0.55*	0.98*	0.34	1.35*	
Wiggins2	Original sample	1	19	12.0	0.47 b (0.43–0.50)	0.70 b (0.59–0.8)	0.17 a (0.12–0.23)	0.91 b (0.77–1.05)	
		2	17	21.3	0.60 a (0.56–0.63)	0.89 a (0.78–1.0)	0.20 a (0.15–0.26)	1.16 a (1.02–1.31)	
	Test sample	1	7	17.0	0.49*	0.61*	0.23*	1.02*	
		2	3	29.0	0.62*	0.73	0.32	1.30*	
Yuma	Original sample	1	6	19.9	0.76 b (0.63–0.87)	0.78 b (0.57–0 .99)	0.29 b (0.10–0.48)	1.04 b (0.64–1.43)	
		2	7	27.0	0.93 ab (0.81–1.05)	1.04 ab (0.85–1.23)	0.41 a (0.24–0.59)	1.50 ab (1.13–1.87)	
		3	7	37.2	1.05 a (0.93–1.16)	1.34 a (1.15–1.53)	0.54 a (0.36–0.71)	2.01 a (1.64–2.38)	
	Test sample	1	5	17.1	0.52	0.59*	0.16*	0.96*	
		2	2	27.6	0.58	0.80*	0.29*	1.14*	
		3	3	40.4	0.99*	1.20*	0.50*	1.93*	

 $^{^{}m a}$ Values within a column and within the same field followed by the same letters are not significantly different (P < 0.05).

EC_s zones, which was probably due to the low level of SOM in these fields.

Comparison between foc and Kd of EPTC, Metribuzin, and Metolachlor in Test Sites with Original Sites. Ten additional samples were taken from each field to determine whether the differences in f_{oc} and K_d for EPTC, metribuzin, and metolachlor between EC_s zones within each field held for other areas of the same field. The location of these sites were chosen based on the pattern of the ECs zones within each field, and we attempted to take samples from EC_s zones that, in some cases, were isolated from the major delineation of that zone and were surrounded by a different EC_s zone (Figure 1). Although an attempt was made to sample all of the EC_s zones from areas that had not been previously sampled (Figure 1), closer examination of the coordinates of the sites after the soil had been taken revealed that test samples from Wiggins1 were only taken from EC_s zones 1 and 2.

In Wiggins 1, the average f_{oc} and the $K_{\rm d}$ for EPTC and for metolachlor in the two EC_s zones fell within the 95%

Table 3. Pearson correlation coefficients (r values) of parameters measured in Wiggins1, CO.3

	$K_{ m d}$						
Parameter	EC_a	EPTC	Metribuzin	Metolachlor	f_{oc}		
EC _a K _d	1.00	0.84	0.73	0.85	0.92		
EPTC Metribuzin Metolachlor		1.00	0.75 1.00	0.93 0.84 1.00	0.79 0.74 0.82		
f_{oc}					1.00		

^a Abbreviations: NC, parameters that were not correlated at the P < 0.05 level of significance; EC_a , soil apparent electrical conductivity; f_{oc} , fraction soil organic carbon; K_d , herbicide-partition coefficient.

confidence limit of the values in the original samples (Table 2). The average K_d for metribuzin did not fall within the 95% confidence limit of the original samples' values. In Wiggins 2, the average f_{oc} and the K_d for metolachlor in the two EC_s zones fell within the 95% confidence limit of the values in the original samples (Table 2). The average K_d for EPTC and for metribuzin in zone 1 were within the 95% confidence limit of the original samples, but they were outside this confidence interval for zone 2 (Table 2). In Yuma, the average f_{oc} in zone 3, but not in zones 1 or 2, was within the 95% confidence interval of the original samples (Table 2). However, the average K_d for EPTC, for metribuzin, and for metolachlor all fell within the 95% confidence interval of the original samples for each of the three zones (Table 2).

These results support the observation that the different EC_s zones within each field do represent different levels of f_{oc} and, consequently, the binding of EPTC, metribuzin, and metolachlor. However, the relationships between f_{oc} and K_d for the herbicides in the test sample sites and the original sample sites were not perfect. This could be because of the way in which we

Table 4. Pearson correlation coefficients (r values) of parameters measured in Yuma, CO.^a

			$K_{ m d}$				
Parameter	EC_a	EPTC	Metribuzin	Metolachlor	f_{oc}		
EC _a K _d	1.00	0.67	NC	0.62	0.80		
EPTC Metribuzin Metolachlor		1.00	0.77 1.00	0.98 0.84 1.00	0.75 NC 0.69		
foc					1.00		

 $^{^{\}rm a}$ Abbreviations: NC, parameters that were not correlated at the P < 0.05 level of significance; EC_a , soil apparent electrical conductivity; f_{oc} , fraction soil organic carbon; K_d, herbicide-partition coefficient.

^b Values in parentheses are the 95% confidence interval for each measurement.

c An asterisk (*) indicates mean value falls within the 95% confidence limit of an EC class within each field.

Table 5. Pearson correlation coefficients (r values) of parameters measured in Yuma, CO.^a

Parameter	EC_a	EPTC	Metribuzin	Metolachlor	f_{oc}
EC _a K _d	1.00	0.67	NC	0.62	0.80
EPTC Metribuzin Metolachlor		1.00	0.77 1.00	0.98 0.84 1.00	0.75 NC 0.69
foc					1.00

^a Abbreviations: NC, parameters that were not correlated at the P < 0.05 level of significance; EC_a, soil apparent electrical conductivity; f_{oc} , fraction soil organic carbon; $K_{\rm d}$, herbicide-partition coefficient.

chose the test sample sites. We attempted to sample areas of the field where one EC_s zone was surrounded by another EC_s zone. Because the mapping of ECs zones is not perfect, it is likely that some of the test sample site were not correctly identified.

Predicting K_d for EPTC, Metribuzin, and Metolachlor within EC_s Zones. The range of the K_d for EPTC, for metribuzin, and for metolachlor in each of the test samples from the different zones in the three fields was estimated using the published average K_{oc} for each herbicide (Weber et al. 2000) and the range of f_{oc} values in each EC_s zone based on the original samples from each zone. The predicted range of K_d values for all three herbicides were clearly different between zones in each field and, in most cases, did not overlap (Table 6). There was more overlap in the actual range of K_d values from the test samples in each of the zones in the three fields for the three herbicides. In Wiggins2, there was no difference between the K_d values for EPTC between the two EC_s zones (Table 6). In Yuma, there was a clear difference in the K_d values for all three herbicides between zones 1 and 3 (Table 6).

The actual and predicted ranges of $K_{\rm d}$ values overlapped in six out of seven cases for metolachlor and five out of seven cases for metribuzin (Table 6). For EPTC, there was good overlap between the actual and predicted $K_{\rm d}$ values in Wiggins1, but there was no overlap in the predicted and actual $K_{\rm d}$ values for any of the zones in Wiggins2 or Yuma (Table 6). In these cases, the predicted $K_{\rm d}$ values for EPTC were always higher than the actual values. The average K_{oc} for EPTC across these three fields was lower than the published K_{oc} values (147 vs. 200), and this difference contributed to the overestimation of the $K_{\rm d}$ for EPTC.

Because the test samples were taken from sites within EC_{s} zones in the fields that had not been previously sampled, these

results suggest that one can reasonably predict the $K_{\rm d}$ value for metribuzin and metolachlor within an EC_s zone based on the range of f_{oc} within each zone and that one could create a map of the average $K_{\rm d}$ values for these herbicides based on an EC_a map of the field. The results are not so clear with EPTC. However, the predicted $K_{\rm d}$ values for EPTC could be used to delineate areas of a field with different levels of binding of EPTC for modeling purposes, although the predicted values may overestimate binding.

Conclusion

These results support the conclusions reached by Jaynes et al. (1995b) who proposed that EC_a maps could be used to map the variability of K_d for atrazine across a field. Our results show that the same is true for metribuzin and metolachlor, and possibly, for EPTC.

The work done in this study differed from that done by Jaynes et al. (1995b) in that, in the latter study, 117 samples were taken on a 250- by 250-m grid in a 32-ha field. In this study, only 20 to 38 samples were taken per field based on zone sampling, and yet, we were able to reasonably predict the range of K_d values of metribuzin, and metolachlor, and possibly, EPTC within each zone based on these few samples. The advantage of using an EC_a map to detect soil variability at the field level is the density of the data and the ability to create zones within a field. Our data show that one can predict the f_{oc} of a zone based on a relatively small number of samples taken from each zone. This soil property, in turn, could be used to predict the relative sorption of herbicides within each zone based on published K_{oc} values. Previous attempts to map the binding of herbicides have been done at much larger scales compared with this work. By using soil ECa maps and directed sampling, one could create a map of the K_d for herbicides that can be used to model the variability in the movement and dissipation of the herbicide across a field. Additionally, there is the potential to use such maps to create a variable rate-application map for soil-applied herbicides. Further research will need to be done to determine if such an approach is feasible and economical.

Sources of Materials

- ¹ Veris Technologies, Inc., 601 N. Broadway, Salina, KS 67401.
- ² AgGPS Parallel Swathing Option, Trimble Navigation Ltd., 9290 Bond Street, Suite 102, Overland Park, KS 66214.

Table 6. Comparison of measured vs. predicted values for K_d for EPTC, metribuzin, and metolachlor taken from additional sites in three fields in Colorado based on K_d = $(f_{oc} \times K_{oc})/100$. a,b

		$K_{ m d}$						
		EPTC		Metr	ibuzin	Metolachlor		
Field	Zone	Actual range	Predicted range	Actual range	Predicted range	Actual range	Predicted range	
				L	kg ⁻¹			
Wiggins1	1	0.44-0.78	0.69-0.93	0.16-0.22	0.13-0.17	0.68-1.45	0.69-0.90	
	2	0.65 - 2.23	1.03-1.28	0.24-0.56	0.19 - 0.22	1.08-2.91	1.04-1.26	
Wiggins2	1	0.52-0.79	0.86-0.99	0.17 - 0.34	0.16-0.19	0.83 - 1.36	0.83 - 1.01	
	2	0.67 - 0.71	1.12-1.27	0.25-0.38	0.21 - 0.23	1.03-1.35	1.11-1.26	
Yuma	1	0.38-0.78	1.27-1.74	0.04-0.29	0.23 - 0.32	0.58-1.29	1.26-1.74	
	2	0.62-0.98	1.62-2.10	0.24-0.35	0.30-0.39	0.84-1.44	1.62-2.09	
	3	1.11-1.32	1.86-2.31	0.42-0.64	0.34-0.43	1.66-2.26	1.86-2.37	

^a Abbreviations: K_d , herbicide-partition coefficient; $f_{o\phi}$ soil organic matter; $K_{o\phi}$ organic carbon partition coefficient.

^b K_{oc} values used were the literature values for these herbicides (Weber et al. 2000) (EPTC, 200; Metribuzin, 60; Metolachlor, 200).

- ³ AgGPS 132, Trimble Navigation Ltd., 9290 Bond Street Suite 102, Overland Park, KS 66214.
- ⁴ SAS, 2001. SAS/STAT User's guide. Release 8.00. SAS Institute Inc., 100 SAS Campus Drive, Cary, NC 27513.
 - ⁵ ESRI, One International Court Broomfield, CO 80021.
- ⁶ Leco-CHN 1000, LECO Corporation, 3000 Lakeview Avenue, St. Joseph, MI 49085.
- ⁷ Analytical grade EPTC, metolachlor, metribuzin, and butylate were purchased from Aldrich Chemical Co., P.O. Box 355, Milwaukee, WI 53201.
- ⁸ Corex glass centrifuge tube Fisher Scientific, 4500 Turnberry Drive, Hanover Park, IL 60103.
- ⁹ Hewlett-Packard 5890 gas chromatograph, HP-5972 mass quadrupole, Alltech Associates, Inc., 2051 Waukegan Road, Deerfield, IL 60015.
- ¹⁰ Alltech Associates, Inc., 2051 Waukegan Road, Deerfield, IL 60015.
- ¹¹ SyStat ver. 3.5, Systat Software Inc. 501 Canal Blvd., Suite C, Point Richmonds, CA 94804.

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